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(54) 【発明の名称】 珪化物焼結体

(57) 【要約】

【課題】 熱処理した鋼の切削等に必要な耐摩耗性を具え、鋼等の加工コストを低減させることのできる、結合材を用いて焼結した珪化物焼結体を提供する。

【解決手段】 Alと、周期律表IaおよびIIa族から選ばれる一つの元素Mと、珪素とからなる珪化物を含む珪化物焼結体である。この珪化物焼結体は、組成が $Alx \pm 1M_{y \pm 1}Si_{z \pm 1}$ で表される珪化物が50～75体積%と残部が結合相と不可避不純物とからなる。この結合相はIIa、V a、VIa族金属の炭化物、窒化物、炭窒化物および珪化物から選ばれる少なくとも1種またはこれらの固溶体化合物からなる。 $Alx \pm 1M_{y \pm 1}Si_{z \pm 1}$ で表される珪化物は焼結体組織中で前記結合相を介して相互に接合されている。

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【特許請求の範囲】

【請求項1】 Alと、周期律表Ia族およびIIa族から選ばれる一つの元素Mと、硼素とからなる硼化物を含む硼化物焼結体であって、

前記硼化物焼結体は、組成が $Al_x \leq 1$ 、 $M_y \leq 1$ 、 $B_z \geq 1$ で表される硼化物が50～75体積%と残部が結合相と不可避不純物とからなり、

前記結合相はI Va、Va、VIa族金属の炭化物、窒化物、炭窒化物および硼化物から選ばれる少なくとも1種またはこれらの固溶体化合物からなり、

$Al_x \leq 1$ 、 $M_y \leq 1$ 、 $B_z \geq 1$ で表される硼化物が焼結体組織中で前記結合相を介して相互に接合されていることを特徴とする硼化物焼結体。

【請求項2】 上記元素MがMgであることを特徴とする請求項1に記載の硼化物焼結体。

【請求項3】 上記元素MがLiであることを特徴とする請求項1に記載の硼化物焼結体。

【請求項4】 上記結合相がTi、Zrの炭化物、窒化物、炭窒化物の少なくとも一種を主体とすることを特徴とする請求項1に記載の範囲の硼化物焼結体。

【請求項5】 組成が $Al_x \leq 1$ 、 $M_y \leq 1$ 、 $B_z \geq 1$ で表される硼化物が $5 \mu m$ 以下の粒子からなることを特徴とする請求項1に記載の硼化物焼結体。

【請求項6】 不可避不純物として、Alの酸化物、元素Mの酸化物、Bの酸化物およびAl、元素MおよびBの複合酸化物から選択される少なくとも1種を含むことを特徴とする請求項1に記載の硼化物焼結体。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は耐摩耗材料や切削工具に好適な硼化物焼結体に関するものである。特に、鋼や鋳鉄の加工・耐摩工具や切削工具に最適な高硬度の硼化物焼結体に関するものである。

【0002】

【従来の技術】切削工具に用いられる Al_2O_3 や Si_3N_4 からなるセラミック工具は硬度がHv1600～2400と高く、鉄系材料の切削においては良好な耐摩耗性を示すが、靱性に乏しい。そのため、被削性の良い鋳鉄の切削には使用されるが、鋼の切削においては耐欠損性の低下により十分な寿命を得られていない。

【0003】また、超硬合金工具は、その焼結体硬度がHv1500～2000とセラミックより低く、さらに金属Coを含むため、熱処理によりHRC40程度まで高硬度化させた鋼の切削においては耐摩耗性、耐欠損性に劣り、十分な工具寿命が得られない。

【0004】一方、高硬度な切削工具としてcBN焼結体があり、焼き入れによりHRC50以上に高硬度化された焼入鋼の切削においては高い性能を示すことが知られている。また、cBN焼結体はHRC30～50の一般的な熱処理鋼の切削でも、セラミック工具や超硬合金工具と同等以上の

寿命を持つ。しかし、製造コストの高い超高压高温発生装置を用いて超高压下で合成されるcBNを原料としており、さらに超高压下で焼結されるために工具単価が高く、加工コストが高くなるために一般的に使用されていない。

【0005】これに対し、H.WerheitらのJournal of Alloys and Compounds, 202 (1993) 269-281には、Alを含む3元硼化物として、 $AlLiB_{14}$ の単結晶の硬度がHv2950、 $AlMgB_{14}$ の単結晶の硬度がHv2790と高い硬度を有することが示されている。この論文は、多量のアルミニウム融液中にマグネシウムと硼素を溶解し、結晶を析出させる方法を開示している。

【0006】また、別の従来技術としてUSP6099605に記載の技術が知られている。この公報はAl、Mg、B元素の粉末を化学量論組成で配合後、メカニカルアロイング法を用いて微細化した後に、30重量%のTiB₂を加えてホットプレスで焼結することにより、Hv3800-4600の高硬度焼結体を得られることを示している。

【0007】

20 【発明が解決しようとする課題】しかし、上記の論文とUSPに開示される技術では次のような問題があった。前記論文の技術では、緻密で不純物の少ない焼結体を得ることができないという問題がある。この論文の技術は、数十 μm 以上の $AlMgB_{14}$ 粒子が生成できる。より具体的には、粒径が最小でも50 μm であり、最大では2mmに達する。しかし、 $AlMgB_{14}$ は脆焼結性であり、このような粗粒の粉末からは緻密な焼結体を得ることができない。

【0008】また、このような粗粒を微細化し、高压高温装置を用いれば緻密な焼結体を得ることができる。しかし、粗粒を粉砕するには微細化に長時間を要し、粉砕容器や粉砕媒体（ボールなど）から不純物が3重量%以上と多量に混入して、組成の制御が困難である。さらに、このようにして得られた焼結体は靱性が低いため、HRC40以上の硬度を有する鋼材では連続切削を行っても欠損が生じて十分な性能を得られない。

【0009】一方、USP6099605に記載の技術では、不純物の混入により十分な硬度と靱性をもつ焼結体を得ることができないという問題がある。鋼製の粉砕ボールとAl、Mg、Bの原料粉末を入れた高エネルギータイプの粉砕装置でメカニカルアロイングを行なうため、粉砕ボールや容器材質の不純物混入が避けられない。そのため、鉄と原料硼素が反応して、 FeB_{14} が生成し混入していることが確認されている。このような鉄の硼化物は脆性材料であると共に鋼材との反応性が高いため、この焼結体を切削工具として用いた場合に刃先の耐摩耗性と耐欠損性のいずれをも低下させる問題がある。

【0010】また、メカニカルアロイングでは酸化反応が生じやすく、さらに急激な酸化反応による爆発の恐れがあるために、LiやNa等のIa、IIa族金属を含む混合原料を微細化して焼結体を得ることは実質的に不可能であ

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る。

【0011】従って、本発明の主目的は、熱処理した鋼の切削等に必要な耐摩耗性を見え、鋼等の加工コストを低減させることのできる、結合材を用いて焼結した碳化物焼結体を提供することにある。

【0012】

【課題を解決するための手段】本発明は、結合材の組成や原料の粒径を規定することで上記の目的を達成する。

【0013】すなわち、本発明の碳化物焼結体は、Alと、周期律表IaおよびIIa族から選ばれる一つの元素Mと、酸素とからなる碳化物を含む碳化物焼結体である。前記碳化物焼結体は、組成が $Al_{x \leq 1} M_{y \leq 1} B_{z \geq 12}$ で表される碳化物が50〜75体積%と残部が結合相と不可避不純物とからなる。前記結合相はIVa、Va、VIa族金属の炭化物、窒化物、炭窒化物および碳化物から選ばれる少なくとも1種またはこれらの固溶体化合物からなる。そして、 $Al_{x \leq 1} M_{y \leq 1} B_{z \geq 12}$ で表される碳化物が焼結体組織中で前記結合相を介して相互に接合されていることを特徴とする。

【0014】従来、組成が $Al_{x \leq 1} M_{y \leq 1} B_{z \geq 12}$ で表される碳化物を含む焼結体は、不可避不純物を除いて $Al_{x \leq 1} M_{y \leq 1} B_{z \geq 12}$ のみからなる焼結体であるか、重量%で30%の添加物を含む焼結体で高い硬度を得られるが、十分な強度が得られない。例えば、USP6099605に記載の技術では、メカニカルアロイングにより各原料粉末の結晶構造を完全に破壊するような粉砕を行うため、粉砕容器・媒体から脱化をもたらず不純物が混入するからである。また、メカニカルアロイング後に30重量%のTiB₂を配合し、高硬度の焼結体となるが、TiB₂は体積%で17%と少なく、難焼結性の $Al_{x \leq 1} M_{y \leq 1} B_{z \geq 12}$ 碳化物粒子同士が接触してしまい十分な結合強度が得られないためである。

【0015】本発明では、三元碳化物の含有量を50〜75体積%とし、残部の25〜50体積%を結合材とすることで、結合相を介して三元碳化物間を強い強度で結合させる。特に、結晶構造の崩れていない微細な三元碳化物粉末を原料として用い、その難焼結性を改善する。その結果、切削工具に適する高い硬度と耐欠損性を見える焼結体を得ることができる。

【0016】本発明焼結体は、 $Al_{x \leq 1} M_{y \leq 1} B_{z \geq 12}$ で表される50〜75体積%の三元碳化物と残部を結合相と不可避不純物とからなる。より具体的な三元碳化物の組成としてはAlMgB₁₄やAlLiB₁₄などが挙げられる。AlMgB₁₄の場合、より正確な構造はAl_{0.75}Mg_{0.75}B₁₄である。

【0017】結合相としては、IVa、Va、VIa族金属の炭化物、窒化物、炭窒化物、碳化物から選ばれる1種もしくは混合物あるいは固溶体化合物からなる。より具体的にはTi、Zrの炭化物、窒化物、炭窒化物、碳化物の少なくとも一種を含むものが好ましい。

【0018】不可避不純物としては、一般にAlMgB₁₄を

含む系では、AlおよびMgの酸化物、MgAl₂O₄ならびに結合相金属元素の酸化物が見られる。AlLiB₁₄を含む系では、AlおよびLiの酸化物、AlLiO₂ならびに結合相金属元素の酸化物が見られる。

【0019】焼結体を構成する三元碳化物の最大粒径は5μm以下が好ましい。このような微細な三元碳化物で焼結体を構成することにより、鋼の切削における耐摩耗性と耐欠損性を得るに必要な強度を有する焼結体となる。より好ましい三元碳化物の最大粒径は2μm以下である。また、切削工具として好ましい焼結体の硬度はHv25GPa以上である。

【0020】上記の碳化物焼結体は、最大粒径が5μm以下の碳化物粒子を圧力：150MPa以上10GPa以下、温度：1000℃以上1500℃以下で焼結することで得られる。より好ましい碳化物粒子の最大粒径は3μm以下である。

【0021】微細な碳化物粒子を用いることで、緻密で高硬度の焼結体を得ることができる。このような碳化物粒子は、粉砕を行わないか短時間の粉砕とすることで結晶構造を極力崩さず、かつ不純物の少ない状態とすることができる。焼結圧力のより好ましい範囲は、1GPa以上5GPa以下、更に好ましくは、1GPa以上3GPa以下である。焼結温度のより好ましい範囲は1200〜1400℃である。焼結保持時間は、15〜60分程度が好ましい。

【0022】焼結体の原料粉末となる微細な碳化物粒子は、粉砕を行うことなく当初から微粒の碳化物粒子を得る方法と、まず粗粒を得て、その後粉砕することで微粒とする方法の2通りがある。

【0023】粉砕を行わない方法は、酸素：最大粒径3μm以下で75〜91原子%、Al：4〜21原子%、周期律表IaおよびIIa族から選ばれる一つの元素M：3〜6原子%の組成を有する原料を、窒素以外の不活性ガス雰囲気中で、1300℃以下の温度で加熱処理する工程により得ることができる。

【0024】最大粒径が3μm以下の酸素を原料とすることで、得られる碳化物粒子の最大粒径を5μm以下に抑えることができる。より好ましくは、最大粒径が1μm以下の酸素を原料とし、得られる碳化物粒子の最大粒径を3μm以下とする。

【0025】従来、AlMgB₁₄では、結晶成長させるためにAlが多く含まれていた。例えばAlの含有量は80〜91原子%程度である。本発明では、極力Alの含有量を減らし、微細な碳化物粒子が得られる組成を選択した。Alが21原子%を超えると結晶粒成長が速く、粗粒の碳化物粒子となる傾向がある。

【0026】AlMgB₁₄について、Alの含有量を変化させて上記の方法にて微粒の碳化物粒子が得られた組成例を表1に示す。この表1における組成No.1はAlMgB₁₄の化学量論組成で、微細な碳化物粒子が得られたが、若干の酸化物も見られた。また、No.2は得られた粒子が微粒であり、酸化物も非常に少なく好ましいAlMgB₁₄であっ

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た。さらに、N₂でも微粒のAlMgB₁₄が合成できたが、N₂ *【0027】
o.2に比べて粗粒化しており、好ましい微粒子が得られ 【表1】
るAl量としては21原子%と思われる。 *

No	at%				wt% (左記 at%の換算)			
	B	Al	Mg	合計	B	Al	Mg	合計
1	90.15	4.83	5.02	100	79.43	10.62	9.95	100
2	86.00	9.21	4.79	100	71.81	19.19	8.99	100
3	76.55	20.24	4.21	100	55.74	37.27	6.99	100

【0028】加熱処理の雰囲気は、不活性ガス雰囲気とする。ただし、窒素は除く。通常、アルゴンを用いることが好適である。

【0029】加熱処理温度は、理論上、Alの融点(660.4℃)以上の温度〜1300℃以下の温度であれば良い。1300℃を超える温度で合成した場合はAlB₁₂も同時に合成してしまうため好ましくない。最適な合成温度は1200〜1300℃、特に1200℃前後である。保持時間は、30〜90分程度が好ましい。

【0030】この方法であれば、粉碎を行うことなく微粒の碳化物粒子を得ることができ、粉碎時に不純物が混入して焼結体とした際に碳化物の含有量が低下することを回避できる。

【0031】次に、粉碎を行う方法は、まず原料：最大粒径40μm以下で75〜91原子%、Al：4〜21原子%、周期律表IaおよびIIa族から選ばれる一つの元素M：3〜6原子%の組成を有する原料を、窒素以外の不活性ガス雰囲気中にて、1300℃以下の温度で加熱処理し、最大粒径が50μm以下で、かつ平均粒径15μm以下の碳化物粒子を得る。続いて、この最大粒径が50μm以下の碳化物粒子を粉碎して最大粒径5μm以下の碳化物粒子とする。

【0032】原料の組成、加熱処理における雰囲気、温度は粉碎を行わない方法の場合と同様である。ここでは原料となる原料の粒径が粗いため合成された碳化物粒径も大きくなるが、最大粒径が50μm以下で、平均粒径を15μm以下とすることで、粉碎工程を用いても短時間で最大粒径5μm以下に微細化できる。粉碎時間が短かければ、不純物の混入がほとんど無い状態で碳化物粉末を得ることができる。そして、不純物の少ない碳化物粒子を用いることで焼結性も改善され、緻密な焼結体を得ることができる。

【0033】粉碎は、極力不純物が混入しないような条件を選択して行うことが好ましい。ボールミルを用いた粉碎条件例としては、ボール：アルミナ製、直径3〜6mm、粉碎時間：4〜10時間が挙げられる。できるだけ、短時間で粉碎を行うことが好ましい。

【0034】

【発明の実施の形態】以下、本発明の実施の形態を説明する。

(実施例1) 純度99.9%、最大粒径3μm以下の無定形原料粉末、純度99.9%、最大粒径40μm以下のアルミニウム

10μm粉末、純度99.9%、最大粒径180μm以下のマグネシウム粉末をそれぞれ85原子%、10原子%、5原子%配合混合した。この混合粉末を高純度なアルミナるつぽにいれ、高温雰囲気加熱炉中に設置し、99.99%以上の高純度アルゴンガス雰囲気中、1200℃で1時間保持し、最大粒径が5μmで平均粒径が2μmのAlMgB₁₄粉末を得た。また、上記と同様に純度99.9%、最大粒径1μm以下の無定形原料粉末とすることにより、最大粒径で2μm、平均粒径で0.7μmのAlMgB₁₄粉末を得た。

【0035】上記の各々の粒子を用いて、表2に示す組成で最大粒径で3μm以下のTiN粒子を配合した。これらの混合粉末をアルミナ製のボールミル容器中に、アルミナ製ボール、エタノールとともに充填してボールミルし、均質に混合した。この混合粉末を1×10⁻³Paの真空中、600℃で乾燥処理したのち、ペレット状に加圧成形した。この成形体をMo容器中に入れ、この容器を高圧高温装置を用いて、圧力2GPa、温度1350℃で30分間保持して焼結体を得た。得られた焼結体のX線回折測定結果とビッカース硬度の測定結果も表2に示す。X線回折測定の結果、全ての焼結体において、AlMgB₁₄とTiN、TiB₂が観察された。これらの物質以外には、MgAl₂O₄とAl₂O₃のピークが認められた焼結体もあった。

【0036】次に、これらの焼結体の組織を走査型電子顕微鏡で観察したところ、微細なAlMgB₁₄粒子は結合相を介して相互に接合していることが認められた。

【0037】比較例として、上記の方法で結合材を含まない焼結体(比較例1-7)、さらに結合材として、TiNを10体積%、20体積%含む焼結体(比較例1-8、1-9)を作製した。これらのX線回折測定結果、硬度測定結果も表2に示す。また、走査型電子顕微鏡で組織を観察したところ、結合材を含む場合でもAlMgB₁₄が相互に接触している箇所が多く、粒子間の三重点に結合材の多くが存在していた。

【0038】上記焼結体を切れ刃とする切削加工用チップを製作した。これらの切削加工用チップを用いて、熱処理した炭素鋼SCr435 (HRC30)の丸棒(φ150×300mm)の外周切削を20分間行った。切削条件はV=300m/min、d=0.5mm、f=0.2mm/rev、乾式である。20分切削後の本発明例と比較例の逃げ面摩耗量の結果を表2に示す。

【0039】

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【表2】

		AlMgB ₁₄ の粒度 最大[平均] (μm)	配合組成 (体積%)	X線回折測定結果	硬度 (GPa)	逃げ面 摩耗量 (mm)
本 発 明 例	1-1	2[0.7]	52AlMgB ₁₄ , 48TiN	AlMgB ₁₄ , TiN, TiB ₂ , MgAl ₂ O ₃ , Al ₂ O ₃	26.0	0.105
	1-2	2[0.7]	60AlMgB ₁₄ , 40TiN	AlMgB ₁₄ , TiN, TiB ₂ , MgAl ₂ O ₃ , Al ₂ O ₃	26.5	0.102
	1-3	2[0.7]	70AlMgB ₁₄ , 30TiN	AlMgB ₁₄ , TiN, TiB ₂ , MgAl ₂ O ₃ , Al ₂ O ₃	26.8	0.124
	1-4	5[2]	66AlMgB ₁₄ , 45TiN	AlMgB ₁₄ , TiN, TiB ₂ , MgAl ₂ O ₃	27.0	0.080
	1-5	5[2]	60AlMgB ₁₄ , 40TiN	AlMgB ₁₄ , TiN, TiB ₂ , MgAl ₂ O ₃	30.2	0.109
	1-6	5[2]	76AlMgB ₁₄ , 25TiN	AlMgB ₁₄ , TiN, TiB ₂ , MgAl ₂ O ₃ , Al ₂ O ₃	30.5	0.099
比 較 例	1-7	2[0.7]	100AlMgB ₁₄	AlMgB ₁₄ , MgAl ₂ O ₃ , Al ₂ O ₃	32.0	0.165
	1-8	5[2]	90AlMgB ₁₄ , 10TiN	AlMgB ₁₄ , TiN, TiB ₂ , MgAl ₂ O ₃ , Al ₂ O ₃	32.0	0.160
	1-9	5[2]	80AlMgB ₁₄ , 20TiN	AlMgB ₁₄ , TiN, TiB ₂ , MgAl ₂ O ₃	30.6	0.172

【0040】表2から明らかなように、本発明例はいずれも25GPa以上の硬度と少ない逃げ面摩耗量を具えており、優れた硬度を有する焼結体であることがわかる。

【0041】(実施例2) 最大粒径で2 μm 以下のAlMgB₁₄粒子と最大粒径で3 μm 以下の結合材粒子を表3に示す組成で配合した。これらの混合粉末を実施例1と同様にして高压高温焼結して焼結体を得た。得られた焼結体のX線回折測定結果とビッカース硬度の測定結果を表3に示す。全ての焼結体において、AlMgB₁₄と配合した結合材と結合材を形成する金属元素の硼化物が観察された。上記の物質以外に、MgAl₂O₃とAl₂O₃のピークが認められた。

【0042】比較例として、表3に示すように、結合材*

		配合組成 (体積%)		X線回折測定結果	硬度 (GPa)	欠損寿命 (分)
		AlMgB ₁₄	結合材			
本 発 明 例	2-1	50	50TiC	AlMgB ₁₄ , TiC, TiB ₂ , MgAl ₂ O ₃	28.0	11
	2-2	60	40ZrC	AlMgB ₁₄ , ZrC, ZrB ₂ , MgAl ₂ O ₃ , Al ₂ O ₃	30.6	13
	2-3	55	45ZrN	AlMgB ₁₄ , ZrN, ZrB ₂ , MgAl ₂ O ₃ , Al ₂ O ₃	25.8	16
	2-4	65	45TiCN	AlMgB ₁₄ , TiCN, TiN, TiB ₂ , MgAl ₂ O ₃	26.0	12
	2-5	70	30TiC, 10TiB ₂	AlMgB ₁₄ , TiC, TiB ₂ , MgAl ₂ O ₃	31.3	18
	2-6	64	28TiB ₂ , 18TiCN	AlMgB ₁₄ , TiCN, TiN, TiB ₂ , MgAl ₂ O ₃ , Al ₂ O ₃	28.0	18
	2-7	60	40WC, 10TiC	AlMgB ₁₄ , WC, TiC, TiB ₂ , (V,Ti)C, MgAl ₂ O ₃ , Al ₂ O ₃	25.2	21
	2-8	65	20HfC, 10TiC, 5TiB ₂	AlMgB ₁₄ , HfC, TiC, HfB ₂ , TiB ₂ , MgAl ₂ O ₃	34.2	20
比 較 例	2-9	42	45TiB ₂ , 25TiN	AlMgB ₁₄ , TiN, TiB ₂ , AlN, AlB ₃	19.0	1
	2-10	77	10ZrN, 18TiCN	AlMgB ₁₄ , ZrN, (Zr,Ti)N, TiC, TiB ₂ , MgAl ₂ O ₃	33.0	6
	2-11	80	12HfC, 8TiN	AlMgB ₁₄ , HfC, TiB ₂ , MgAl ₂ O ₃	37.2	4
	2-12	90	5TiCN, 3TiB ₂ , ZrC	AlMgB ₁₄ , TiC, TiN, TiB ₂ , V, AlN, MgAl ₂ O ₃	28.0	0.2

【0045】表3から明らかなように、本発明例はいずれも25GPa以上の硬度を具え、さらに欠損寿命も長く、硬度と靱性を兼備した焼結体であることがわかる。

【0046】(実施例3) 硼素とアルミニウムとリチウムの組成比が82原子%、13原子%、5原子%となるように、純度99.9%、最大粒径1 μm 以下の結晶硼素粉末と、純度99.9%、最大粒径で300 μm 以下のアルミニウム-28原子%リチウム合金粉末とをそれぞれ70重量%と30重量%配合して混合した。この混合粉末を高純度なアルミナるつぽに入れ、高温昇昇気加熱炉中に設置し、99.99%以上の高純度アルゴンガス昇昇気中、1180℃で1時間保持し最大粒径で2 μm 、平均粒径で0.8 μm のAlLiB₁₄粉末を得た。

*の配合比を50体積%以上の焼結体(比較例2-9)と10~23体積%(比較例2-10~2-12)とした焼結体も作製した。

【0043】上記焼結体を切れ刃とする切削加工用チップを作製した。これらの切削加工用チップを用いて、熱処理した炭素鋼SCM435(HRC30)の丸棒($\phi 150 \times 300 \text{mm}$)に4本のV字溝を入れた被削材を準備し、断続切削を行なった。切削条件はV=250 mm/min 、d=0.2 mm 、f=0.15 mm/rev 、乾式である。本発明例と比較例の工具の欠損寿命を表3に示す。

【0044】

【表3】

※【0047】この粉末に、表4に示す組成で最大粒径で2 μm 以下のZrN粒子を配合した。これらの混合粉末をジルコニア製のボールミル容器中、ジルコニア製ボール、エタノールとともに充填してボールミルし、均質に混合した。この混合粉末を $1 \times 10^{-3} \text{Pa}$ の真空中、600℃で乾燥処理したのち、ペレット状に加圧成形した。この成形体をMo容器に入れ、この容器を高压高温装置を用いて、圧力2GPa、温度1400℃で30分間保持して焼結体を得た。得られた焼結体のX線回折測定結果とビッカース硬度の測定結果を表4に示す。全ての焼結体において、AlLiB₁₄とZrN、ZrB₂が観察された。上記の物質以外に、AlLiO₃とAl₂O₃のピークが認められた。

※50 【0048】次に、これらの焼結体の組織を走査型電子

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顕微鏡で観察したところ、 AlLiB_4 粒子は結合相を介して相互に接合していることが認められた。

【0049】比較例として、上記の方法で結合材を含まない焼結体（比較例3-5）、さらに結合材としてZrNを20体積%含む焼結体（比較例3-6）を作製した。これらのX線回折測定結果、硬度測定結果も表4に示す。

【0050】上記焼結体を切れ刃とする切削加工用チップ*

プを作製した。これらの切削加工用チップを用いて、熱処理した炭素鋼SCM435（HRC30）の丸棒（ $\phi 150 \times 300 \text{ mm}$ ）の連続切削を10分間行なった。切削条件は $V=400 \text{ m/min}$ 、 $d=0.2 \text{ mm}$ 、 $f=0.15 \text{ mm/rev}$ 、乾式である。本発明例と比較例の刃先損傷の結果を表4に示す。

【0051】

【表4】

		配合組成 (体積%)	X線回折測定結果	硬度 (GPa)	逃げ面 摩耗量 (mm)
本 発 明 例	3-1	50 AlLiB_4 , 50ZrN	AlLiB_4 , ZrN, ZrB_2	27.5	0.130
	3-2	60 AlLiB_4 , 40ZrN	AlLiB_4 , ZrN, ZrB_2 , AlLiO_2 , Al_2O_3 , ZrO ₂	30.2	0.142
	3-3	70 AlLiB_4 , 30ZrN	AlLiB_4 , ZrN, ZrB_2 , AlLiO_2 , Al_2O_3	33.6	0.161
	3-4	73 AlLiB_4 , 27ZrN	AlLiB_4 , ZrN, ZrB_2 , AlLiO_2 , Al_2O_3	32.7	0.179
比 較 例	3-5	100 AlLiB_4	AlLiB_4 , AlLiO_2 , AlB_3 , AlB_5	30.0	8分で摩耗 大きく欠損
	3-6	80 AlLiB_4 , 20ZrN	AlLiB_4 , ZrN, ZrB_2 , AlLiO_2	31.8	0.250

【0052】表4から明らかなように、本発明例はいずれも25GPa以上の硬度と少ない逃げ面摩耗量を具えており、優れた硬度を有する焼結体であることがわかる。

【0053】

※【発明の効果】以上説明したように、本発明焼結体は、組成が $\text{Al}_x\text{Li}_y\text{B}_z$ で表される硼化物が結合材により相互に結合された組織とすることで、切削工具として用いた場合に優れた耐摩耗性と耐久損性とを備える。

※20

フロントページの続き

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4G001 BA01 BA03 BA05 BA06 BA24
BA25 BA26 BA37 BA38 BA39
BA43 BA44 BA45 BA57 BB01
BB03 BB05 BB06 BB24 BB25
BB26 BB37 BB38 BB39 BB43
BB44 BB45 BB57 BC13 BD12
BD18

CLAIMS

[Claim(s)]

[Claim 1] aluminum. One element M chosen from a periodic-table Ia group and an IIa group. Boron. It is the boride sintered compact equipped with the above. the aforementioned boride sintered compact 50 - 75 volume % and the remainder consist [the boride to which composition is expressed with $AlX \leq 1My \leq 1BZ \geq 12$] of a binder phase and an unescapable impurity. The aforementioned binder phase consists of at least one sort chosen from the carbide of IVa, Va, and a VIa group metal, a nitride, a charcoal nitride, and a boride, or these solid-solution compounds. It is characterized by joining mutually the boride expressed with $AlX \leq 1My \leq 1BZ \geq 12$ through the aforementioned binder phase all over a sintered-compact organization.

[Claim 2] The boride sintered compact according to claim 1 characterized by the above-mentioned element M being Mg.

[Claim 3] The boride sintered compact according to claim 1 characterized by the above-mentioned element M being Li.

[Claim 4] The boride sintered compact of the range according to claim 1 with which the above-mentioned binder phase is characterized by the thing of the carbide of Ti and Zr, a nitride, and a charcoal nitride for which a kind is made into a subject at least.

[Claim 5] The boride sintered compact according to claim 1 with which the boride to which composition is expressed with $AlX \leq 1My \leq 1BZ \geq 12$ is characterized by the bird clapper from a particle 5 micrometers or less.

[Claim 6] The boride sintered compact according to claim 1 characterized by including at least one sort chosen from the multiple oxide of the oxide of aluminum, the oxide of Element M, the oxide of B and aluminum, and Elements M and B as an unescapable impurity.

[Translation done.]

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs] this invention relates to the suitable boride sintered compact for antifriction material or a cutting tool. Especially, it is related with the optimal boride sintered compact of a high degree of hardness for processing and abrasion-resistant tool, and cutting tool of steel or cast iron.

[0002]

[Description of the Prior Art] The ceramic tool which consists of aluminum $2O_3$ used for a cutting tool or Si_3N_4 is lacking in toughness, although a degree of hardness is high and indicates good abrasion resistance to be Hv 1600-2400 in cutting of iron system material. Therefore, although used for cutting of cast iron with sufficient machinability, in cutting of steel, sufficient life has not been acquired by the fall of deficit-proof nature.

[0003] Moreover, in cutting of the steel which made it form into a high degree of hardness to about 40 HRc with heat treatment since the sintered-compact degree of hardness of a cemented carbide tool was lower than Hv 1500-2000 and a ceramic and it contained Metal Co further, it is inferior to abrasion resistance and deficit-proof nature, and sufficient tool life is not acquired.

[0004] on the other hand -- high -- there is a cBN sintered compact as a degree of hardness cutting tool, and it is known that a high performance is shown in cutting of the hardening steel formed into the high degree of hardness by 50 or more HRc(s) with quenching. Moreover, a cBN sintered compact has a ceramic tool, a cemented carbide tool, and a life more than equivalent also for cutting of the common heat treatment steel of HRc 30-50. However, cBN compounded under extra-high voltage using extra-high voltage thermogenesis equipment with a high manufacturing cost is used as the raw material, and, generally [since it is further sintered under extra-high voltage, a tool unit price is high, and / since processing cost becomes high] it is not used.

[0005] On the other hand, H. Werheit's and others Journal of Alloys and Compounds and 202 (1993) 269-281 that the degree of hardness of the single crystal of Hv2950 and AlMgB14 has [the degree of hardness of the single crystal of AlLiB14] Hv2790 and a high degree of hardness as a 3 yuan boride containing aluminum. This paper dissolves magnesium and boron into a lot of aluminum melts, and the method of depositing a crystal is indicated.

[0006] Moreover, the technology of a publication is known by USP6099605 as another conventional technology. After this official report turns the powder of aluminum, Mg, and B element minutely after combination using the mechanical alloying method by the stoichiometric composition, by adding 30% of the weight of TiB₂, and sintering with a hotpress shows that the high degree-of-hardness sintered compact of Hv 3800-4600 is obtained.

[0007]

[Problem(s) to be Solved by the Invention] However, there were the following problems with the technology indicated by above paper and USP. With the technology of the aforementioned paper, there is a problem that it is precise and a sintered compact with few impurities cannot be obtained. The technology of this paper can generate AlMgB14 particle dozens of micrometers or more. More specifically, the minimum is also 50 micrometers and particle size amounts to 2mm at the maximum. However, AlMgB14 is a difficulty degree of sintering, and cannot obtain a precise sintered compact from the powder of such coarse grain.

[0008] Moreover, such coarse grain is turned minutely, and if high-pressure elevated-temperature equipment is used, a precise sintered compact can be obtained. However, for grinding coarse grain, detailed-ization takes a long time, an impurity mixes in 3 % of the weight or more and a large quantity from a pulverization container or tumbling medias (ball etc.), and control of composition is difficult. Furthermore, in the steel materials which have a 40 or more-HRc degree of hardness, since the sintered compact obtained by doing in this way has low toughness, even if it performs continuation cutting, a deficit arises and it cannot obtain sufficient performance.

[0009] On the other hand, with the technology of a publication, the problem referred to as being unable to obtain the sintered compact equipped with a sufficient degree of hardness and sufficient toughness by mixing of an impurity is in USP6099605. In order for the

pulverization equipment of the high-energy type into which a steel crushing steel ball and the raw material powder of aluminum, Mg, and B were put to perform mechanical alloying, impurity mixing of a crushing steel ball or the container quality of the material is not avoided. Therefore, it is checked that iron and raw material boron react, and FeB₄9 is generating and mixing. When this sintered compact is used as a cutting tool since reactivity with steel materials is high while the boride of such iron was a brittle material, it has the problem on which both the abrasion resistance of the edge of a blade and deficit-proof nature are reduced.

[0010] Moreover, since there is fear of explosion by still more rapid oxidation reaction, it is [that it is easy to produce oxidation reaction in mechanical alloying] substantially impossible to turn minutely the mixed raw material containing Ia(s), such as Li and Na, and an IIa group metal, and to obtain a sintered compact.

[0011] Therefore, the key objective of this invention is to offer the boride sintered compact which it can have [sintered compact] abrasion resistance required for cutting of the heat-treated steel etc., and can reduce processing costs, such as steel, and which was sintered using binding material.

[0012]

[Means for Solving the Problem] this invention attains the above-mentioned purpose by specifying composition of binding material, and the particle size of a raw material.

[0013] That is, the boride sintered compact of this invention is a boride sintered compact containing the boride which consists of aluminum, and one element M chosen from a periodic table Ia and an IIa group and boron. As for the aforementioned boride sintered compact, 50 - 75 volume % and the remainder consist [the boride to which composition is expressed with $AlX \leq 1My \leq 1BZ = 12$] of a binder phase and an unescapable impurity. The aforementioned binder phase consists of at least one sort chosen from the carbide of IVa, Va, and a VIa group metal, a nitride, a charcoal nitride, and a boride, or these solid-solution compounds. And it is characterized by joining mutually the boride expressed with $AlX \leq 1My \leq 1BZ = 12$ through the aforementioned binder phase all over a sintered-compact organization.

[0014] Conventionally, sufficient intensity is not obtained, although the sintered compact containing the boride to which composition is expressed with $AlX \leq 1My \leq 1BZ = 12$ is a sintered compact which consists only of $AlX \leq 1My \leq 1BZ = 12$ except for an unescapable impurity or a high degree of hardness can be obtained with the sintered compact which contains 30% of additive by weight %. For example, with technology given in USP6099605, it is because the impurity which brings about an embrittlement from a pulverization container and a medium mixes in order to perform pulverization which destroys the crystal structure of each raw material powder completely by mechanical alloying. Moreover, although 30% of the weight of TiB₂ is blended after mechanical alloying and it becomes the sintered compact of a high degree of hardness, it is because there is little TiB₂ at volume % as 17%, the $AlX \leq 1My \leq 1BZ = 12$ boride particles of a difficulty degree of sintering contact and sufficient bond strength is not obtained.

[0015] By this invention, between 3 yuan borides is combined by strong intensity through a binder phase by making the content of a boride of 3 yuan into 50 to 75 volume %, and making 25 - 50 volume % of the remainder into binding material. The difficulty degree of sintering is improved using the detailed 3 yuan boride powder with which the crystal

structure has not collapsed especially as a raw material. Consequently, the high degree of hardness suitable for a cutting tool and a sintered compact equipped with deficit-proof nature can be obtained.

[0016] this invention sintered compact consists of a binder phase and an unescapable impurity the 3 yuan boride of 50 expressed with $AlX \leq 1$ $My \leq 1$ $BZ \geq 12$ - 75 volume %, and the remainder. As composition of a boride, AlMgB14, AlLiB14 of 3 more concrete yuan, etc. are mentioned. In AlMgB14, more exact structure is aluminum0.75Mg 0.78B14.

[0017] It consists of one sort, the mixture, or the solid-solution compound chosen from the carbide of IVa, Va, and a VIa group metal, a nitride, a charcoal nitride, and a boride as a binder phase. The thing of the carbide of Ti and Zr, a nitride, a charcoal nitride, and a boride which contains a kind at least is more specifically desirable.

[0018] ~~As an unescapable impurity,~~ the oxide of a binder-phase metallic element is looked at by the oxide of aluminum and Mg, and MgAl2O4 row by the system which generally contains AlMgB14. The oxide of a binder-phase metallic element is looked at by the oxide of aluminum and Li, and AlLiO2 row by the system containing AlLiB14.

[0019] The maximum droplet size of the 3 yuan boride which constitutes a sintered compact has desirable 5 micrometers or less. By constituting the sintered compact of such 3 detailed yuan from a boride, it becomes the sintered compact which has intensity required to obtain the abrasion resistance and deficit-proof nature in cutting of steel. The maximum droplet size of a more desirable 3 yuan boride is 2 micrometers or less.

Moreover, the degree of hardness of a sintered compact desirable as a cutting tool is more than Hv25GPa.

[0020] The above-mentioned boride sintered compact is obtained because a maximum droplet size sinters a boride particle 5 micrometers or less less than [more than pressure:150MPa10GPa] and less than [more than temperature:1000 degree-C1500 degree C]. The maximum droplet size of a more desirable boride particle is 3 micrometers or less.

[0021] By using a detailed boride particle, the precise sintered compact of a high degree of hardness can be obtained. Such a boride particle cannot break down the crystal structure as much as possible because it considers [whether it grinds and] as short-time pulverization, and it can make it a state with few impurities. The more desirable range of 1 or more-GPa 5 or less GPa of a sintering pressure is 3 or less GPa more than per GPa still more preferably. The more desirable range of sintering temperature is 1200-1400 degrees C. The sintering holding time has about 15 - 60 desirable minutes.

[0022] The detailed boride particle used as the raw material powder of a sintered compact has two kinds, the method of obtaining the boride particle of a particle from the beginning, without grinding, and the method of making it into a particle by obtaining coarse grain first and grinding after that.

[0023] The method which does not grind can be acquired according to the process which heat-treats the raw material which has composition of one element M:3 chosen from 75 to 91 atom %, four to aluminum:21 atom %, a periodic table Ia, and an IIa group by 3 micrometers or less of boron:maximum droplet sizes - 6 atom % at the temperature of 1300 degrees C or less in inert gas atmosphere other than nitrogen.

[0024] The maximum droplet size of the boride particle obtained can be held down to 5 micrometers or less because a maximum droplet size uses boron 3 micrometers or less as

a raw material. More preferably, a maximum droplet size uses boron 1 micrometer or less as a raw material, and sets the maximum droplet size of the boride particle obtained to 3 micrometers or less.

[0025] Conventionally, in AlMgB14, in order to carry out a crystal growth, many aluminum was contained. For example, the content of aluminum is a 80 - 91 atom % grade. In this invention, the content of aluminum was reduced as much as possible, and the composition from which a detailed boride particle is obtained was chosen. If aluminum exceeds 21 atom %, a grain growth will happen, and there is an inclination used as the boride particle of coarse grain.

[0026] The example of composition from which the content of aluminum was changed and the boride particle of a particle was obtained by the above-mentioned method about AlMgB14 is shown in Table 1. Some oxide was also seen, although composition No.1 in this table 1 is the stoichiometric composition of AlMgB14 and the detailed boride particle was obtained. Moreover, the obtained particle was a particle and No.2 were desirable AlMgB14 also with very little oxide. Furthermore, although No.3 have compounded AlMgB14 of a particle, it has coarse-grain-ized compared with No.2, and 21 atom % is thought as an amount of aluminum from which a desirable particle is obtained.

[0027]

[Table 1]

[0028] Atmosphere of heat-treatment is made into inert gas atmosphere. However, nitrogen is removed. Usually, it is suitable to use an argon.

[0029] Heat-treatment temperature should just be the temperature not more than temperature -1300 degree C beyond the melting point (660.4 degrees C) of aluminum theoretically. It is not desirable in order to compound AlB12 simultaneously, when it compounds at the temperature exceeding 1300 degrees C. 1200-1300 degrees C especially of optimal synthetic temperature are before and after 1200 degrees C. About 30 - 90 minutes of the holding time are desirable.

[0030] When it was this method, and the boride particle of a particle can be obtained, an impurity mixes at the time of trituration and it considers as a sintered compact, without grinding, it can avoid that the content of a boride falls.

[0031] Next, the method of grinding heat-treats the raw material which has composition of one element M:3 first chosen from 75 to 91 atom %, four to aluminum:21 atom %, a periodic table Ia, and an IIa group by 40 micrometers or less of boron:maximum droplet sizes - 6 atom % at the temperature of 1300 degrees C or less in inert gas atmosphere other than nitrogen, and a maximum droplet size is 50 micrometers or less, and it obtains the boride particle of 15 micrometers or less of mean particle diameters. Then, this maximum droplet size grinds a boride particle 50 micrometers or less, and considers as the boride particle of 5 micrometers or less of maximum droplet sizes.

[0032] The atmosphere in composition of a raw material and heat-treatment and temperature are the same as that of the case of the method which does not grind. Although the boride particle size compounded since the particle size of boron used as a

raw material was coarse also becomes large here, even if a maximum droplet size uses a trituration process by setting a mean particle diameter to 15 micrometers or less by 50 micrometers or less, -izing can be carried out [detailed] to 5 micrometers or less of maximum droplet sizes for a short time. Trituration time can obtain boride powder in short ***** and the state where there is almost no mixing of an impurity. And a degree of sintering is also improved by using a boride particle with few impurities, and a precise sintered compact can be obtained.

[0033] It is desirable to perform trituration by choosing conditions which an impurity does not mix as much as possible. As an example of a trituration condition using the ball mill, product made from ball:alumina, diameter [of 3-6mm], and trituration time: 4 - 10 hours are mentioned. As much as possible, grinding for a short time is desirable.

[0034]

[Embodiments of the Invention]-Hereafter, the gestalt of operation of this invention is explained.

(Example 1) the magnesium dust of 99.9% of purity, the amorphous boron powder of 3 micrometers or less of maximum droplet sizes, 99.9% of purity, the aluminium powder of 40 micrometers or less of maximum droplet sizes, 99.9% of purity, and 180 micrometers or less of maximum droplet sizes -- respectively -- 85 atom % and ten atom % -- pentatomic % combination mixture was carried out This end of mixed powder was put into the high grade alumina crucible, and it installed into the elevated-temperature atmosphere heating furnace, and held at 1200 degrees C for 1 hour among 99.99% or more of high grade argon gas atmosphere, and the maximum droplet size obtained AlMgB14 powder whose mean particle diameter is 2 micrometers by 5 micrometers. Moreover, by considering as 99.9% of purity, and the amorphous boron powder of 1 micrometer or less of maximum droplet sizes like the above, 2 micrometers was obtained by the maximum droplet size, and AlMgB14 0.7-micrometer powder was obtained by the mean particle diameter.

[0035] The TiN particle 3 micrometers or less was blended by the maximum droplet size by the composition shown in Table 2 using each above-mentioned particle. The ball mill of these end of mixed powder was filled up with and carried out with the ball made from an alumina, and ethanol into the ball mill container made from an alumina, and it mixed homogeneously. After carrying out dryness processing of this end of mixed powder at 600 degrees C among the vacuum of 1×10 to 3 Pa, pressing was carried out to the shape of a pellet. This Plastic solid was put in into Mo container, this container was held for 30 minutes at pressure 2GPa and the temperature of 1350 degrees C using high-pressure elevated-temperature equipment, and the sintered compact was obtained. The X diffraction measurement result of a sintered compact and the measurement result of Vickers hardness which were obtained are also shown in Table 2. In all sintered compacts, AlMgB14, TiN, and TiB2 were observed as a result of X diffraction measurement. In addition to the matter of ***** , there was also a sintered compact with which the peak of MgA1204 and A1203 was accepted.

[0036] Next, when gazed at the organization of these sintered compacts with the scanning electron microscope, having joined AlMgB14 detailed particle mutually through a binder phase was admitted.

[0037] the sintered compact (example 1-7 of comparison) which does not contain binding material by the above-mentioned method as an example of comparison -- 10 volume %

and the sintered compact (the example 1-8 of comparison, 1-9) 20 volume % included were further produced for TiN as a binding material. These X diffraction measurement results and a determination-of-hardness result are also shown in Table 2. Moreover, even when it was gazed at with an organization with a scanning electron microscope and binding material was included, there were many parts where AlMgB14 touches mutually, and many of binding material existed in the triple point between particles.

[0038] The chip for cutting which uses the above-mentioned sintered compact as a cutting edge was manufactured. Periphery cutting of the round bar ($\phi 150 \times 300 \text{ mm}$) of the heat-treated carbon steel SCN 435 (HRC30) was performed for 20 minutes using these chips for cutting. Cutting conditions are $V=300 \text{ m/min}$, $d=0.5 \text{ mm}$, $f=0.2 \text{ mm/rev}$, and dry type. The result of the amount of flank wears of the example of this invention after 20-minute cutting and the example of comparison is shown in Table 2.

[0039]

[Table 2]

[0040] Each example of this invention is equipped with the degree of hardness of 25 or more GPa, and the few amount of flank wears, and it turns out that it is the sintered compact which has the outstanding degree of hardness so that clearly from Table 2.

[0041] (Example 2) It blended by the composition which shows a binding-material particle 3 micrometers or less in Table 3 by AlMgB14 particle and a maximum droplet size 2 micrometers or less by the maximum droplet size. High-pressure elevated-temperature sintering of these end of mixed powder was carried out like the example 1, and the sintered compact was obtained. The X diffraction measurement result of a sintered compact and the measurement result of Vickers hardness which were obtained are shown in Table 3. In all sintered compacts, the boride of the metallic element which forms the binding material blended with AlMgB14 and binding material was observed. In addition to the above-mentioned matter, the peak of MgAl_2O_4 and Al_2O_3 was accepted.

[0042] As an example of comparison, as shown in Table 3, the sintered compact more than 50 volume % (example 2-9 of comparison) and the sintered compact made into ten to 23 volume % (example 2-10 to 2-12 of comparison) also produced the compounding ratio of binding material.

[0043] The chip for cutting which uses the above-mentioned sintered compact as a cutting edge was manufactured. The $\phi 150 \times 300 \text{ mm}$ material which put four V character slots into the round bar ($\phi 150 \times 300 \text{ mm}$) of the heat-treated carbon steel SCN 435 (HRC30) was prepared using these chips for cutting, and intermittent cutting was performed. Cutting conditions are $V=250 \text{ m/min}$, $d=0.2 \text{ mm}$, $f=0.15 \text{ mm/rev}$, and dry type. The deficit life of

the tool of the example of this invention and the example of comparison is shown in Table 3.

[0044]

[Table 3]

[0045] Each example of this invention is equipped with the degree of hardness of 25 or more GPa, a deficit life is also still longer, and it turns out that it is the sintered compact which combined a degree of hardness and toughness so that clearly from Table 3.

[0046] (Example 3) By 99.9% of purity, and the maximum droplet size, the aluminum-28 atom % lithium alloy-powder end of 300 micrometers or less was blended with 70 % of the weight 30% of the weight, respectively, and it mixed with 99.9% of purity, and the crystal boron powder of 1 micrometer or less of maximum droplet sizes so that the composition ratio of boron, aluminum, and a lithium might become 82 atom %, 13 atom %, and pentatomic %. It held at 1180 degrees C for 1 hour among 99.99% or more of high grade argon gas atmosphere by putting this end of mixed powder into a high grade alumina crucible, and installing into an elevated-temperature atmosphere heating furnace, and 2 micrometers was obtained by the maximum droplet size, and AlLiB14 0.8-micrometer powder was obtained by the mean particle diameter.

[0047] The ZrN particle 2 micrometers or less was blended with this powder by the maximum droplet size by the composition shown in Table 4. The ball mill of these end of mixed powder was filled up with and carried out with the ball made from a zirconia, and ethanol among the ball mill container made from a zirconia, and it mixed homogeneously. After carrying out dryness processing of this end of mixed powder at 600 degrees C among the vacuum of 1×10^{-3} to 3 Pa, pressing was carried out to the shape of a pellet. This Plastic solid was put in into Mo container, this container was held for 30 minutes at pressure 2GPa and the temperature of 1400 degrees C using high-pressure elevated-temperature equipment, and the sintered compact was obtained. The X diffraction measurement result of a sintered compact and the measurement result of Vickers hardness which were obtained are shown in Table 4. AlLiB14, ZrN, and ZrB2 were observed in all sintered compacts. In addition to the above-mentioned matter, the peak of AlLiO 2 and Al₂O₃ was accepted.

[0048] Next, when gazed at the organization of these sintered compacts with the scanning electron microscope, having joined AlLiB14 particle mutually through a binder phase was admitted.

[0049] The sintered compact (example 3-5 of comparison) which does not contain

binding material by the above-mentioned method as an example of comparison, and the sintered compact (example 3-6 of comparison) which 20 volume % Contains ZrN as a binding material further were produced. These X diffraction measurement results and a determination-of-hardness result are also shown in Table 4.

[0050] The chip for cutting which uses the above-mentioned sintered compact as a cutting edge was manufactured. Continuation cutting of the round bar ($\phi 150 \times 300 \text{ mm}$) of the heat-treated carbon steel SCN 435 (HRC30) was performed for 10 minutes using these chips for cutting. Cutting conditions are $V=400 \text{ m/min}$, $d=0.2 \text{ mm}$, $f=0.15 \text{ mm/rev}$, and dry type. The result of the edge-of-a-blade injury on the example of this invention and the example of comparison is shown in Table 4.

[0051]

[Table 4]

[0052] Each example of this invention is equipped with the degree of hardness of 25 or more GPa, and the few amount of flank wears, and it turns out that it is the sintered compact which has the outstanding degree of hardness so that clearly from Table 4.

[0053]

[Effect of the Invention] As explained above, this invention sintered compact is that the boride to which composition is expressed with $\text{AlX} \leq 1 \text{ M} \leq 1 \text{ BZ} \leq 12$ considers as the organization mutually combined by binding material, and is equipped with the abrasion resistance and deficit-proof nature which were excellent when it used as a cutting tool.

[Translation done.]

TECHNICAL FIELD

[The technical field to which invention belongs] this invention relates to the suitable boride sintered compact for antifriction material or a cutting tool. Especially, it is related with the optimal boride sintered compact of a high degree of hardness for processing and abrasion-resistant tool, and cutting tool of steel or cast iron.

[Translation done.]

PRIOR ART

[Description of the Prior Art] The ceramic tool which consists of aluminum $2O_3$ used for a cutting tool or Si_3N_4 is lacking in toughness, although a degree of hardness is high and indicates good abrasion resistance to be Hv 1600-2400 in cutting of iron system material. Therefore, although used for cutting of cast iron with sufficient machinability, in cutting of steel, sufficient life has not been acquired by the fall of deficit-proof nature.

[0003] Moreover, in cutting of the steel which made it form into a high degree of hardness to about 40 HRC with heat treatment since the sintered-compact degree of hardness of a cemented carbide tool was lower than Hv 1500-2000 and a ceramic and it contained Metal Co further, it is inferior to abrasion resistance and deficit-proof nature, and sufficient tool life is not acquired.

[0004] on the other hand -- high -- there is a cBN sintered compact as a degree of hardness cutting tool, and it is known that a high performance is shown in cutting of the hardening steel formed into the high degree of hardness by 50 or more HRC(s) with quenching. Moreover, a cBN sintered compact has a ceramic tool, a cemented carbide tool, and a life more than equivalent also for cutting of the common heat treatment steel of HRC 30-50. However, cBN compounded under extra-high voltage using an extra-high voltage elevated-temperature generator with a high manufacturing cost is used as the raw material, and, generally [since it is further sintered under extra-high voltage, a tool unit price is high, and / since processing cost becomes high] it is not used.

[0005] On the other hand, H. Werheit's and others Journal of Alloys and It is shown in Compounds and 202 (1993) 269-281 that the degree of hardness of the single crystal of Hv2950 and AlMgB14 has [the degree of hardness of the single crystal of AlLiB14] Hv2790 and a high degree of hardness as a 3 yuan boride containing aluminum. This paper dissolves magnesium and boron into a lot of aluminum melts, and the method of depositing a crystal is indicated.

[0006] Moreover, the technology of a publication is known by USP6099605 as another conventional technology. After this official report turns the powder of aluminum, Mg, and B element minutely after combination using the mechanical alloying method by the stoichiometric composition, by adding 30% of the weight of TiB_2 , and sintering with a hotpress shows that the high degree-of-hardness sintered compact of Hv 3800-4600 is obtained.

[Translation done.]

EFFECT OF THE INVENTION

[Effect of the Invention] As explained above, this invention sintered compact is that the boride to which composition is expressed with $AlX \leq 1$ $My \leq 1$ $BZ \geq 12$ considers as the organization mutually combined by binding material, and is equipped with the abrasion resistance and deficit-proof nature which were excellent when it used as a cutting tool.

[Translation done.]

TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] However, there were the following problems with the technology indicated by above paper and USP. With the technology of the aforementioned paper, there is a problem that it is precise and a sintered compact with few impurities cannot be obtained. The technology of this paper can generate AlMgB14 particle dozens of micrometers or more. More specifically, the minimum is also 50 micrometers and particle size amounts to 2mm at the maximum. However, AlMgB14 is a difficulty degree of sintering, and cannot obtain a precise sintered compact from the powder of such coarse grain.

[0008] Moreover, such coarse grain is turned minutely, and if high-pressure elevated-temperature equipment is used, a precise sintered compact can be obtained. However, for grinding coarse grain, detailed-ization takes a long time, an impurity mixes in 3 % of the weight or more and a large quantity from a pulverization container or tumbling medias (ball etc.), and control of composition is difficult. Furthermore, in the steel materials which have a 40 or more-HRc degree of hardness, since the sintered compact obtained by doing in this way has low toughness, even if it performs continuation cutting, a deficit arises and it cannot obtain sufficient performance.

[0009] On the other hand, with the technology of a publication, the problem referred to as being unable to obtain the sintered compact equipped with a sufficient degree of hardness and sufficient toughness by mixing of an impurity is in USP6099605. In order for the pulverization equipment of the high-energy type into which a steel crushing steel ball and the raw material powder of aluminum, Mg, and B were put to perform mechanical alloying, impurity mixing of a crushing steel ball or the container quality of the material is not avoided. Therefore, it is checked that iron and raw material boron react, and FeB49 is generating and mixing. When this sintered compact is used as a cutting tool since reactivity with steel materials is high while the boride of such iron was a brittle material, it has the problem on which both the abrasion resistance of the edge of a blade and deficit-proof nature are reduced.

[0010] Moreover, since there is fear of explosion by still more rapid oxidation reaction, it is [that it is easy to produce oxidation reaction in mechanical alloying] substantially impossible to turn minutely the mixed raw material containing Ia(s), such as Li and Na, and an IIa group metal, and to obtain a sintered compact.

[0011] Therefore, the key objective of this invention is to offer the boride sintered compact which it can have [sintered compact] abrasion resistance required for cutting of the heat-treated steel etc., and can reduce processing costs, such as steel, and which was sintered using binding material.

[Translation done.]

MEANS

[Means for Solving the Problem] this invention attains the above-mentioned purpose by specifying composition of binding material, and the particle size of a raw material.

[0013] That is, the boride sintered compact of this invention is a boride sintered compact containing the boride which consists of aluminum, and one element M chosen from a periodic table Ia and an IIa group and boron. As for the aforementioned boride sintered compact, 50 - 75 volume % and the remainder consist [the boride to which composition is expressed with $AlX \leq 1My \leq 1BZ = 12$] of a binder phase and an unescapable impurity. The aforementioned binder phase consists of at least one sort chosen from the carbide of IVa, Va, and a VIa group metal, a nitride, a charcoal nitride, and a boride, or these solid-solution compounds. And it is characterized by joining mutually the boride expressed with $AlX \leq 1My \leq 1BZ = 12$ through the aforementioned binder phase all over a sintered-compact organization.

[0014] Conventionally, sufficient intensity is not obtained, although the sintered compact containing the boride to which composition is expressed with $AlX \leq 1My \leq 1BZ = 12$ is a sintered compact which consists only of $AlX \leq 1My \leq 1BZ = 12$ except for an unescapable impurity or a high degree of hardness can be obtained with the sintered compact which contains 30% of additive by weight %. For example, with technology given in USP6099605, it is because the impurity which brings about an embrittlement from a trituration container and a medium mixes in order to perform trituration which destroys the crystal structure of each raw material powder completely by mechanical alloying. Moreover, although 30% of the weight of TiB_2 is blended after mechanical alloying and it becomes the sintered compact of a high degree of hardness, it is because there is little TiB_2 at volume % as 17%, the $AlX \leq 1My \leq 1BZ = 12$ boride particles of a difficulty degree of sintering contact and sufficient bond strength is not obtained.

[0015] By this invention, between 3 yuan borides is combined by strong intensity through a binder phase by making the content of a boride of 3 yuan into 50 to 75 volume %, and making 25 - 50 volume % of the remainder into binding material. The difficulty degree of sintering is improved using the detailed 3 yuan boride powder with which the crystal structure has not collapsed especially as a raw material. Consequently, the high degree of hardness suitable for a cutting tool and a sintered compact equipped with deficit-proof nature can be obtained.

[0016] this invention sintered compact consists of a binder phase and an unescapable impurity the 3 yuan boride of 50 expressed with $AlX \leq 1My \leq 1BZ = 12$ - 75 volume %, and the remainder. As composition of a boride, $AlMgB_{14}$, $AlLiB_{14}$ of 3 more concrete yuan, etc. are mentioned. In $AlMgB_{14}$, more exact structure is aluminum0.75Mg0.78B₁₄.

[0017] It consists of one sort, the mixture, or the solid-solution compound chosen from the carbide of IVa, Va, and a VIa group metal, a nitride, a charcoal nitride, and a boride as a binder phase. The thing of the carbide of Ti and Zr, a nitride, a charcoal nitride, and a boride which contains a kind at least is more specifically desirable.

[0018] As an unescapable impurity, the oxide of a binder-phase metallic element is looked at by the oxide of aluminum and Mg, and $MgAl_{12}O_4$ row by the system which

generally contains AlMgB₁₄. The oxide of a binder-phase metallic element is looked at by the oxide of aluminum and Li, and AlLiO₂ row by the system containing AlLiB₁₄.

[0019] The maximum droplet size of the 3 yuan boride which constitutes a sintered compact has desirable 5 micrometers or less. By constituting the sintered compact of such 3 detailed yuan from a boride, it becomes the sintered compact which has intensity required to obtain the abrasion resistance and deficit-proof nature in cutting of steel. The maximum droplet size of a more desirable 3 yuan boride is 2 micrometers or less. Moreover, the degree of hardness of a sintered compact desirable as a cutting tool is more than Hv25GPa.

[0020] The above-mentioned boride sintered compact is obtained because a maximum droplet size sinters a boride particle 5 micrometers or less less than [more than pressure:150MPa10GPa] and less than [more than temperature:1000 degree-C1500 degree C]. The maximum droplet size of a more desirable boride particle is 3 micrometers or less.

[0021] By using a detailed boride particle, the precise sintered compact of a high degree of hardness can be obtained. Such a boride particle cannot break down the crystal structure as much as possible because it considers [whether it grinds and] as short-time trituration, and it can make it a state with few impurities. The more desirable range of 1 or more-GPa 5 or less GPa of a sintering pressure is 3 or less GPa more than per GPa still more preferably. The more desirable range of sintering temperature is 1200-1400 degrees C. The sintering holding time has about 15 - 60 desirable minutes.

[0022] The detailed boride particle used as the raw material powder of a sintered compact has two kinds, the method of obtaining the boride particle of a particle from the beginning, without grinding, and the method of making it into a particle by obtaining coarse grain first and grinding after that.

[0023] The method which does not grind can be acquired according to the process which heat-treats the raw material which has composition of one element M:3 chosen from 75 to 91 atom %, four to aluminum:21 atom %, a periodic table Ia, and an IIa group by 3 micrometers or less of boron:maximum droplet sizes - 6 atom % at the temperature of 1300 degrees C or less in inert gas atmosphere other than nitrogen.

[0024] The maximum droplet size of the boride particle obtained can be held down to 5 micrometers or less because a maximum droplet size uses boron 3 micrometers or less as a raw material. More preferably, a maximum droplet size uses boron 1 micrometer or less as a raw material, and sets the maximum droplet size of the boride particle obtained to 3 micrometers or less.

[0025] Conventionally, in AlMgB₁₄, in order to carry out a crystal growth, many aluminum was contained. For example, the content of aluminum is a 80 - 91 atom % grade. In this invention, the content of aluminum was reduced as much as possible, and the composition from which a detailed boride particle is obtained was chosen. If aluminum exceeds 21 atom %, a grain growth will happen, and there is an inclination used as the boride particle of coarse grain.

[0026] The example of composition from which the content of aluminum was changed and the boride particle of a particle was obtained by the above-mentioned method about AlMgB₁₄ is shown in Table 1. Some oxide was also seen, although composition No.1 in this table 1 is the stoichiometric composition of AlMgB₁₄ and the detailed boride particle was obtained. Moreover, the obtained particle was a particle and No.2 were desirable

AlMgB14 also with very little oxide. Furthermore, although No.3 have compounded AlMgB14 of a particle, it has coarse-grain-ized compared with No.2, and 21 atom % is thought as an amount of aluminum from which a desirable particle is obtained.

[0027]

[Table 1]

[0028] Atmosphere of heat-treatment is made into inert gas atmosphere. However, nitrogen is removed. Usually, it is suitable to use an argon.

[0029] Heat-treatment temperature should just be the temperature not more than temperature -1300 degree C beyond the melting point (660.4 degrees C) of aluminum theoretically. It is not desirable in order to compound AlB12 simultaneously, when it compounds at the temperature exceeding 1300 degrees C. 1200-1300 degrees C especially of optimal synthetic temperature are before and after 1200 degrees C. About 30 - 90 minutes of the holding time are desirable.

[0030] When it was this method, and the boride particle of a particle can be obtained, an impurity mixes at the time of trituration and it considers as a sintered compact, without grinding, it can avoid that the content of a boride falls.

[0031] Next, the method of grinding heat-treats the raw material which has composition of one element M:3 first chosen from 75 to 91 atom %, four to aluminum:21 atom %, a periodic table Ia, and an IIa group by 40 micrometers or less of boron:maximum droplet sizes - 6 atom % at the temperature of 1300 degrees C or less in inert gas atmosphere other than nitrogen, and a maximum droplet size is 50 micrometers or less, and it obtains the boride particle of 15 micrometers or less of mean particle diameters. Then, this maximum droplet size grinds a boride particle 50 micrometers or less, and considers as the boride particle of 5 micrometers or less of maximum droplet sizes.

[0032] The atmosphere in composition of a raw material and heat-treatment and temperature are the same as that of the case of the method which does not grind.

Although the boride particle size compounded since the particle size of boron used as a raw material was coarse also becomes large here, even if a maximum droplet size uses a trituration process by setting a mean particle diameter to 15 micrometers or less by 50 micrometers or less, -izing can be carried out [detailed] to 5 micrometers or less of maximum droplet sizes for a short time. Trituration time can obtain boride powder in short ***** and the state where there is almost no mixing of an impurity. And a degree of sintering is also improved by using a boride particle with few impurities, and a precise sintered compact can be obtained.

[0033] It is desirable to perform trituration by choosing conditions which an impurity does not mix as much as possible. As an example of a trituration condition using the ball mill, product made from ball:alumina, diameter [of 3-6mm], and trituration time: 4 - 10 hours are mentioned. As much as possible, grinding for a short time is desirable.

[0034]

[Embodiments of the Invention] Hereafter, the gestalt of operation of this invention is explained.

(Example 1) the magnesium dust of 99.9% of purity, the amorphous boron powder of 3 micrometers or less of maximum droplet sizes, 99.9% of purity, the aluminium powder of 40 micrometers or less of maximum droplet sizes, 99.9% of purity, and 180 micrometers or less of maximum droplet sizes -- respectively -- 85 atom % and ten atom % -- pentatomic % combination mixture was carried out This end of mixed powder was put into the high grade alumina crucible, and it installed into the elevated-temperature atmosphere heating furnace, and held at 1200 degrees C for 1 hour among 99.99% or more of high grade argon gas atmosphere, and the maximum droplet size obtained AlMgB14 powder whose mean particle diameter is 2 micrometers by 5 micrometers. Moreover, by considering as 99.9% of purity, and the amorphous boron powder of 1 micrometer or less of maximum droplet sizes like the above, 2 micrometers was obtained by the maximum droplet size, and AlMgB14 0.7-micrometer powder was obtained by the mean particle diameter.

[0035] The TiN particle 3 micrometers or less was blended by the maximum droplet size by the composition shown in Table 2 using each above-mentioned particle. The ball mill of these end of mixed powder was filled up with and carried out with the ball made from an alumina, and ethanol into the ball mill container made from an alumina, and it mixed homogeneously. After carrying out dryness processing of this end of mixed powder at 600 degrees C among the vacuum of 1×10^{-3} Pa, pressing was carried out to the shape of a pellet. This Plastic solid was put in into Mo container, this container was held for 30 minutes at pressure 2GPa and the temperature of 1350 degrees C using high-pressure elevated-temperature equipment, and the sintered compact was obtained. The X diffraction measurement result of a sintered compact and the measurement result of Vickers hardness which were obtained are also shown in Table 2. In all sintered compacts, AlMgB14, TiN, and TiB2 were observed as a result of X diffraction measurement. In addition to the matter of *****, there was also a sintered compact with which the peak of MgAl204 and Al203 was accepted.

[0036] Next, when gazed at the organization of these sintered compacts with the scanning electron microscope, having joined AlMgB14 detailed particle mutually through a binder phase was admitted.

[0037] the sintered compact (example 1-7 of comparison) which does not contain binding material by the above-mentioned method as an example of comparison -- 10 volume % and the sintered compact (the example 1-8 of comparison, 1-9) 20 volume % included were further produced for TiN as a binding material These X diffraction measurement results and a determination-of-hardness result are also shown in Table 2. Moreover, even when it gazed at an organization with a scanning electron microscope and binding material was included, there were many parts where AlMgB14 touches mutually, and many of binding material existed in the triple point between particles.

[0038] The chip for cutting which uses the above-mentioned sintered compact as a cutting edge was manufactured. Periphery cutting of the round bar ($\phi 150 \times 300$ mm) of the heat-treated carbon steel SCN 435 (HRC30) was performed for 20 minutes using these chips for cutting. Cutting conditions are $V=300$ m/min, $d=0.5$ mm, $f=0.2$ mm/rev, and dry type. The result of the amount of flank wears of the example of this invention after 20-minute cutting and the example of comparison is shown in Table 2.

[0039]

[Table 2]

[0040] Each example of this invention is equipped with the degree of hardness of 25 or more GPa, and the few amount of flank wears, and it turns out that it is the sintered compact which has the outstanding degree of hardness so that clearly from Table 2.

[0041] (Example 2) It blended by the composition which shows a binding-material particle 3 micrometers or less in Table 3 by AlMgB14 particle and a maximum droplet size 2 micrometers or less by the maximum droplet size. High-pressure elevated-temperature sintering of these end of mixed powder was carried out like the example 1, and the sintered compact was obtained. The X diffraction measurement result of a sintered compact and the measurement result of Vickers hardness which were obtained are shown in Table 3. In all sintered compacts, the boride of the metallic element which forms the binding material blended with AlMgB14 and binding material was observed. In addition to the above-mentioned matter, the peak of $MgAl_2O_4$ and Al_2O_3 was accepted.

[0042] As an example of comparison, as shown in Table 3, the sintered compact more than 50 volume % (example 2-9 of comparison) and the sintered compact made into ten to 23 volume % (example 2-10 to 2-12 of comparison) also produced the compounding ratio of binding material.

[0043] The chip for cutting which uses the above-mentioned sintered compact as a cutting edge was manufactured. The ϕ 150x300mm material which put four V character slots into the round bar (ϕ 150x300mm) of the heat-treated carbon steel SCN 435 (HRC30) was prepared using these chips for cutting, and intermittent cutting was performed. Cutting conditions are $V=250$ m/min, $d=0.2$ mm, $f=0.15$ mm/rev, and dry type. The deficit life of the tool of the example of this invention and the example of comparison is shown in Table 3.

[0044]

[Table 3]

[0045] Each example of this invention is equipped with the degree of hardness of 25 or more GPa, a deficit life is also still longer, and it turns out that it is the sintered compact which combined a degree of hardness and toughness so that clearly from Table 3.

[0046] (Example 3) By 99.9% of purity, and the maximum droplet size, the aluminum-28 atom % lithium alloy-powder end of 300 micrometers or less was blended with 70 % of the weight 30% of the weight, respectively, and it mixed with 99.9% of purity, and the crystal boron powder of 1 micrometer or less of maximum droplet sizes so that the composition ratio of boron, aluminum, and a lithium might become 82 atom %, 13 atom %, and pentatomic %. It held at 1180 degrees C for 1 hour among 99.99% or more of high grade argon gas atmosphere by putting this end of mixed powder into a high grade alumina crucible, and installing into an elevated-temperature atmosphere heating furnace, and 2 micrometers was obtained by the maximum droplet size, and AlLiB14 0.8-micrometer powder was obtained by the mean particle diameter.

[0047] The ZrN particle 2 micrometers or less was blended with this powder by the maximum droplet size by the composition shown in Table 4. The ball mill of these end of mixed powder was filled up with and carried out with the ball made from a zirconia, and ethanol among the ball mill container made from a zirconia, and it mixed homogeneously. After carrying out dryness processing of this end of mixed powder at 600 degrees C among the vacuum of 1×10^{-3} Pa, pressing was carried out to the shape of a pellet. This Plastic solid was put in into Mo container, this container was held for 30 minutes at pressure 2GPa and the temperature of 1400 degrees C using high-pressure elevated-temperature equipment, and the sintered compact was obtained. The X diffraction measurement result of a sintered compact and the measurement result of Vickers hardness which were obtained are shown in Table 4. AlLiB14, ZrN, and ZrB2 were observed in all sintered compacts. In addition to the above-mentioned matter, the peak of AlLiO 2 and Al₂O₃ was accepted.

[0048] Next, when gazed at the organization of these sintered compacts with the scanning electron microscope, having joined AlLiB14 particle mutually through a binder phase was admitted.

[0049] The sintered compact (example 3-5 of comparison) which does not contain binding material by the above-mentioned method as an example of comparison, and the sintered compact (example 3-6 of comparison) which 20 volume % Contains ZrN as a binding material further were produced. These X diffraction measurement results and a determination-of-hardness result are also shown in Table 4.

[0050] The chip for cutting which uses the above-mentioned sintered compact as a cutting edge was manufactured. Continuation cutting of the round bar ($\phi 150 \times 300 \text{ mm}$) of the heat-treated carbon steel SCN 435 (HRC30) was performed for 10 minutes using these chips for cutting. Cutting conditions are $V=400 \text{ m/min}$, $d=0.2 \text{ mm}$, $f=0.15 \text{ mm/rev}$, and dry type. The result of the edge-of-a-blade injury on the example of this invention and the example of comparison is shown in Table 4.

[0051]

[Table 4]

[0052] Each example of this invention is equipped with the degree of hardness of 25 or more GPa, and the few amount of flank wears, and it turns out that it is the sintered compact which has the outstanding degree of hardness so that clearly from Table 4.

[0053]

[Translation done.]